

1 micron = 0,03937 mm
 20 " = 0,7874 mm
 60 " = 2,3622 mm US
 100 " = 3,937 mm
 10 " = 0,3937 mm

1 micron = 10^{-3} mm

1 586 501

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN METAL COATING

(71) We, ALLOY SURFACES COMPANY, INC., a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the chemical vapour diffusion coating of metals to increase their resistance to corrosion and other chemical attacks.

Preliminary diffusion aluminizing of ferrous metals greatly improves the corrosion resistance provided by top coatings. Where the dimensional accuracy of a work-piece is of a high order, such as on the root of a rotor blade that is to be securely received in a socket, it is frequently impractical to permit aluminizing of that root because the added aluminium increases the root's dimensions. Such masking problems arise more frequently with the superalloy components in the hot section of a turbine engine, where aluminizing is more widely practised.

The invention provides a method for localized chemical vapour diffusion coating of metal into a portion of the surface of metal workpiece, which method comprises applying to the workpiece at least one adherent chemical-vapour-deposition-delineating layer that delineates the area of a surface to be diffusion coated, the layer being applied as a slurry of chemical-vapour-diffusion-delineating powder in a solution of a heat-fugitive resin binder in a solvent which is methyl chloroform or methylene chloride permitting the solvent to evaporate to set the layer, and then subjecting the thus-coated workpiece to chemical vapour diffusion coating, e.g. aluminizing.

The term "chemical-vapour-deposition-delineating layer" as used herein includes both a layer which is applied to prevent diffusion coating in the area to which the said layer is applied and, in an alternative embodiment, a layer which contains the metal with which the said portion of the workpiece surface is to be diffusion-coated, whereby the area of the surface covered by the layer becomes diffusion coated with the said metal, during the diffusion coating process.

The layer is preferably covered by another layer which forms a brittle sheath *Hülle* during the diffusion coating process. *"Flöze"*

The sheath-forming layer or one or more of the strata which constitute this layer, preferably have Cr₂O₃, nickel or mixtures of these two, as particles that become coherently united. Neither of these materials contaminate superalloy or stainless steel workpieces inasmuch as only chromium or nickel can be introduced into the work-pieces from these sources, and these two metals are already present in the work-piece. Chromium and nickel are also not considered contaminants for low alloy steels, particularly those ferrous alloys containing at least 1% chromium.

The Cr₂O₃ and nickel particles are so actively effective that they can be diluted with as much as twice their weight of alumina or other inert filler, without losing their sheath-forming ability. While they can be used in undiluted form, it is preferred to dilute these aluminizable ingredients with some filler, at least about half as much filler as active material, by weight. Such dilution diminishes the amount of material that can consume the aluminizing aluminium, and also reduces the masking cost. Moreover, undiluted coatings of Cr₂O₃ and resin tend to crack on drying.

For best masking of those aluminizing diffusions that are conducted at

extremely high temperatures, e.g. 1900°F or higher, it is helpful to have a three-layer masking combination in which the workpiece contacting layer is of the depletion-reducing type, the next layer of the masking type, and the outermost layer of the sheath forming type.

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EXAMPLE 1

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A number of hot section first stage jet engine blades made of B-1900 nickel-base superalloy had their roots dipped in the following mixture:

	Powdered Ni ₃ Al having 20 to 100 micron particle size	111 g.	
10	Powdered chromium having 20 to 100 micron particle size	3.4 g.	10
	Powdered alumina having 20 to 100 micron particle size	111 g.	
	Poly(ethylmethacrylate)	9 g.	
	Methyl chloroform	123 g.	

15 The resin was first dissolved in the methyl chloroform, and the remaining ingredients then added with stirring to form a uniform slurry that did not settle very rapidly. 15

20 A single dip coating treatment with the suspension at room temperature, about 60 to about 80°F, deposited a layer weighing about 130 milligrams per square centimeter after the methyl chloroform solvent had been permitted to evaporate. Only a fraction of a minute was needed to complete such a coating, and it was found to be helpful to repeat the dip several times until the combined coatings weigh about 500 milligrams per square centimeter. Dipping a previously dipped coating in the dispersion does not remove any significant portion of the previous coating, particularly if the previous coating has been permitted to dry at room temperature for about 1/2 minute. 25

After three or more dips as above, the thus-coated blades were dipped in the following coating mixture:

	Powdered nickel, 20 to 100 micron particle size	175 g.	
30	Powdered alumina, 20 to 100 micron particle size	175 g.	30
	Poly(ethylmethacrylate)	4.7 g.	
	Methyl chloroform	62.1 g.	

35 This dipping was repeated two more times, with intervening dryings at least about 1/2 minute long each, to build up an adherent chemical-vapour-deposition-diffusion-delineating layer, weighing about 500 milligrams per square centimeter. In this layer, the nickel functions as a chemical-vapour-diffusion-limiting powder, and the alumina as a diluent. 35

The blades were then promptly inserted in a pre-fired diffusion aluminizing pack having the following composition in parts by weight.

40	Powdered aluminium, 20 to 60 micron particle size	10	} 50 %	40
	Powdered chromium, about 10 micron particle size	40		
	Powdered alumina, 20 to 60 micron particle size	50		
	Powdered NH ₄ Cl	0.3		

45 into which additional NH₄Cl was blended to bring its concentration to the 0.3% value and make up for pre-firing volatilization. All of the blades were completely covered by the pack, and the mass was held in a diffusion coating retort. Diffusion coating was then carried out with a 6 hour hold at 1875°F in the manner described in U.S. Patent No. 3,785,854. The blades were then removed from the cooled retort and carried a hard shell-like sheath or crust where the roots had been covered with the masking dips. These crusts were quite adherent and coherent, so that the aluminizing pack was not materially contaminated by the masking layers, and could be reused for additional aluminizing without further precautions. 50

55 The crusts are fairly brittle and can be readily removed from the blades by light blows of a hammer or even a wood club, or by blasting with an air-propelled stream of nickel shot. The crust fragments are discarded leaving the blade roots showing no aluminizing, and the balance of the blades with a 3 mil aluminized case. 55

The shell or crust formation is due to the fact that the nickel powder in the outermost masking layer undergoes so much aluminizing that these powder particles grow together. The dilution of the nickel with as much as four-thirds its weight of inert material such as alumina does not prevent such growing together.

and neither is it prevented by the presence of the resin in the dipped masking composition. Such resin is completely driven off during the initial portion of the diffusion coating heat, but the relatively small amount of such resin would not significantly affect the results even if it were to survive the diffusion heat or were carbonized by that heat.

The diluted Ni_3Al in the lower layers of masking does not aluminize sufficiently to cause shell or crust formation, even though those layers also contain a small amount of chromium that by itself would form a shell. Any metal-containing layer in contact with a workpiece should contain at least 25% inert non-metal such as the alumina, or kaolin, to assure that the metal or the layer does not sinter to the workpiece, and such dilution also keeps the Ni_3Al from forming a shell or crust.

On the other hand, other aluminizable powders that are essentially inert to the workpiece but form shells, can be used in place of or in addition to the nickel powder in the shell-forming layers. Cr_2O_3 is another such shell-forming material, apparently undergoing some conversion to aluminized metallic chromium. Being less expensive than nickel, Cr_2O_3 is particularly desirable for use where masking expenses are to be minimized. Mixtures of nickel and Cr_2O_3 can be used with an effectiveness corresponding to that of each individually and indeed a small amount, such as 5%, of Ni_3Al can be mixed with the nickel or the Cr_2O_3 without detracting significantly from the results.

All diluents can be omitted from the shell-forming layers, if desired, but this makes it more important to be sure that at least the minimum effective amount of shell-forming layer is applied. In undiluted condition only about 100 milligrams per square centimeter of nickel or Cr_2O_3 is needed, and the presence of the resin adds so little to the shell-forming layer that it has no significant effect on the amount of shell-forming layer needed. Layers deposited from undiluted Cr_2O_3 suspended in a resin solution, tend to crack on drying, whereas there is no such cracking when the Cr_2O_3 is diluted with at least about 1/4 its weight of Al_2O_3 or other diluent.

The resin in the outer layers acts to keep the masking layers from rubbing off onto or into the diffusion coating pack during the packing.

After the first dip or two to apply resin-containing masking layers, some or all subsequent dips can be effected in resin-free suspensions of the coating materials in a solvent that dissolves the resin in the previously applied layers. Inasmuch as coating suspensions entirely free of resin are more difficult to maintain uniform, a little resin or other viscosity-increasing material can be added to such dispersions to reduce the settling rate of the dispersed powders.

It is also helpful to use a combination of shell-forming masking layers in which some are of the type that depend on the presence of nickel powder, and others are of the type that depend on the presence of Cr_2O_3 powder. Thus it is particularly desirable for aluminizings that are effected at about 2000°F or higher, for the shell-forming combination of layers to have the lowermost such layers based on Cr_2O_3 and built up to at least about 300 milligrams per square centimeter, while the uppermost are based on nickel powder and are also built up to at least about 300 milligrams per square centimeter.

While other resins can be used to make the masking layers, the acrylic resins are preferred and poly(ethylmethacrylate) is particularly preferred because it gives such good dip coatings and clean products. Methyl chloroform is a desirable and preferred solvent because it has the desired solvent action combined with good evaporation characteristics and low use hazard. Some acrylic copolymers are not sufficiently soluble in methyl chloroforms, and for such polymers, methylene chloride is used as the solvent.

The composition of the depletion-reducing masking mixture (the lower layer in Example 1) can vary in the manner described in U.S. Patent 3,801,357. Thus the aluminide can be nickel or cobalt aluminide containing between 1/3 and 3/4 atom of aluminium for every atom of nickel or cobalt, the inert particles can range from about 1/4 to about 2/3 of this mixture by weight, and the chromium content can range from about 1/4 to about 3% of this mixture by weight.

The foregoing masking is very effective to prevent the aluminizing of the masked surfaces. It also serves to mask against chromizing.

EXAMPLE 2

A pack having the following composition was used for the chromizing of a PWA 1455 workpiece by embedding the workpiece in the following pack, all percentages being by weight.

Powdered chromium	1.2%	} ca 4 %
Powdered nickel	2.4%	
Powdered aluminum	0.37%	
Powdered alumina	96.03%	

5 All of the powders were minus 325 mesh, their particle sizes ranging from
about 20 to about 50 microns, and the mixture well homogenized with repeated
siftings, then further mixed with 1/2% NH_4Cl and 1/2% MgCl_2 and placed in a
10 chromized steel retort. The packed retort was then covered by an outer retort as
described and illustrated in Patent 3,785,854, care being taken that the outer retort
has no leaks and is well sealed. The atmosphere in the outer retort was displaced by
a stream of argon introduced through an inlet conduit opening near the bottom of
the interior of the outer retort and exited through an outlet conduit opening near
the top of the interior of the outer retort. Heating of the retort was initiated and the
15 flow of argon maintained through the entire heating process at a rate that assured
essentially no entrance of air or moisture into the interior of the retorts. Where the
outer retort has no leaks, an argon flow of about 5 standard cubic feet per hour is
adequate.

The pack was held at 1900 to 1950°F for 30 hours after which heating was
terminated and the retorts permitted to cool, the argon stream being maintained.

20 It can be modified by incorporating in it about 0.1% magnesium.

In general the above pack can have a chromium content of from about 0.6 to
about 2%, a nickel content from about 1/2 to about 3 times the chromium content,
and an aluminum content about 1/10 to about 1/3 the chromium content. The argon
25 atmosphere can be replaced in whole or in part by helium, neon or other inert gas
or mixtures thereof. Other inert diluents like kaolin can be substituted for the
alumina in its pack.

The residue of the diffusion coating pack used above contains a small amount
of nickel-aluminum-chromium alloy and can be utilized as a chemical vapour
diffusion masking mixture in low-temperature aluminizing, that is aluminizing
30 conducted at not over about 1400°F. Thus the used pack can be mixed with 1/5 its
weight of a 6% solution of poly(ethylacrylate) and the mixtures applied by dipping
over the roots of the blades chromized in Example 1, to build up a coating weighing
500 milligrams per square centimeter. The masked blades are then embedded in the
following powder pack, the percentages being by weight:

35 Alumina	85%	35
Aluminum-silicon alloy (88% Al)	15%	

to which is added 1/2% NH_4Cl .

A coating heat in hydrogen with a 30 minute hold at 1350°F deposits a 10
milligram per square centimeter coating over all unmasked surfaces. The blades
40 are then removed from the pack, the masking mixture brushed off, and then heated
in hydrogen having a minus 35°F dew point for 4 hours at 1975°F to diffuse the
aluminum coatings into the surfaces. They are then rapidly air cooled to below
1000°F, aged for 10 hours at 1600 to 1650°F, and again rapidly air cooled to give
blades ready for use with roots only chromized and with their airfoil surfaces
45 chromized and then aluminized.

A particularly desirable masking technique involves the coating of the portions
to be masked with at least one layer of a dispersion of finely divided depletion-
reducing masking solid and resin in the solvent evaporating off sufficient solvent to
set the coating, applying over the set coating at least one stratum of finely divided
50 non-contaminating solid particles that upon aluminizing become coherently held
together to form a secure masking sheath.

The sheath-forming layer or one or more of the strata, which constitute this
layer, preferably have Cr_2O_3 , nickel or mixtures of these two, as the particles that
become coherently united by the aluminizing. Neither of these materials
55 contaminates superalloy or stainless steel workpieces inasmuch as only chromium
or nickel can be introduced into the workpieces from these sources and these two
metals are already present in the workpieces. Chromium and nickel are also not
considered contaminants for low alloy steels, particularly those ferrous alloys
containing at least 1% chromium.

60 The Cr_2O_3 and nickel particles are so actively effective that they can be diluted
with as much as twice their weight of alumina or other inert filler, without losing
their sheath-forming ability. While they can be used in undiluted form, it is

preferred to dilute these aluminizable ingredients with some filler, at least about half as much filler as active material, by weight. Such dilution diminishes the amount of material that can consume the aluminizing aluminum, and also reduces the masking cost. Moreover undiluted coatings of Cr_2O_3 and resin tend to crack on drying. Cr_2O_3 is also not a good shell-former for pack chromizing.

For best masking of diffusion coatings that are applied at extremely high temperatures, e.g. 1900°F or higher, it is helpful to have the masked surface only in contact with an essentially inert layer such as inert diluent, or inert diluent mixed with a small amount, not over about 5% of depletion-preventing material such as powdered chromium. This depletion-preventing material helps keep chromium and other key alloying ingredients of the masked surface from diffusing out of that surface. Such an essentially inert surface-contacting layer is also helpful in the masking of aluminum diffusions that are conducted at temperatures as low as 1100°F.

In another embodiment of the masking method of the invention, a three-layer masking combination is used in which the workpiece-contacting layer is of the essentially inert type, the next layer of the masking type, and the outermost layer of the sheath-forming type. Nickel aluminides present in any masking layer other than a sheath-forming layer, should have no more than about 3 atoms of aluminum for every four atoms of nickel.

To make the masking layers easier to apply, it is helpful to add to the resin solution a little long-chain-hydrocarbon acid such as stearic acid that helps keep the particles of the masking composition dispersed in the volatilizable organic solvent in which they are suspended. As little as about 0.1% of such dispersing aid based on the total weight of the suspension, is enough to impart very good flowability so that the painting, or even dipping of the workpieces, is simpler and produces a more uniform masking layer. However dispersing aid concentrations of at least about 0.3% to about 0.5% are preferred and as much as 1% can be effectively used.

Hydrocarbon chain lengths as short as 12 carbons and as long as 50 carbons or more are suitable for the dispersing aid. Thus lauric acid, myristic acid, oleic acid, and even copolymers of ethylene and acrylic acid, are effective. The dispersing aid should also be soluble in the solvent.

The effectiveness of the dispersing aid is increased by also dissolving in the suspension a small amount of a surface-active agent, preferably a low-foaming non-ionic surface-active agent such as polyethoxyl ether of a linear primary alcohol like cetyl alcohol, or of an alkyl phenol. Only about 0.1% of surface active agent is all that is needed. It should be noted in this connection that the surface-active agent when added without the long-chain-hydrocarbon acid, has substantially no effect on the masking suspension.

The method of the present invention can be used to mask chromizing or to prevent aluminizing. The nickel and/or nickel aluminide in the masking layers combines with either chromium or aluminum or both and in this way prevents significant penetration of either of these metals to the workpiece surface on which the masking is applied.

The essentially inert layer need only weigh about 1/8 gram per square centimeter to improve the masking action by preventing roughening of the workpiece surface being masked. That layer can also weigh as much as about 2 grams per square centimeter, and can be composed of inert materials such as alumina, kaolin or MgO . The presence of about 1/2 to about 5% chromium metal in the essentially inert layer or in the layer above it, contributes a strong depletion-reducing effect.

The following illustrates such a masking technique.

EXAMPLE 3

A group of hot section turbine engine blades of U-520 alloys (0.05% C, 19% Cr, 12% Co, 6% Mo, 1% W, 3% Ti, 2% Al, 0.005% B, the balance Ni) had their roots masked by dipped coating of three superimposed layers as follows:

first layer—a slurry of 2300 grams of 10 to 20 micron particles of alumina in 1300 grams (1000 cc) of a 7% solution of poly(ethylmethacrylate) in methyl chloroform containing 0.5% stearic acid. Three dips were used to provide a layer containing about 350 milligrams of non-volatiles per square centimeter of surface, and the layer was then permitted to dry by exposure to the atmosphere for about 20 seconds.

second layer—a slurry of 20 to 50 micron particles of Ni_3Al , similarly sized particles of Cr and 10 to 20 micron particles of alumina in the foregoing methyl chloroform solution of resin and stearic acid. The slurry contained 50 grams Ni_3Al , 5 grams Cr and 45 grams alumina for every 50 cc. of the foregoing solution, and two dips were used to provide about 400 milligrams of non-volatiles per square centimeter of surface. This layer was then permitted to dry.

third layer—a slurry of 20 to 50 microns particles of Ni, similarly sized particles of Ni_3Al and 10 to 20 micron particles of alumina, suspended in the foregoing methyl chloroform solution of resin and stearic acid. The slurry contained 75 grams Ni, 13 grams Ni_3Al and 12 grams Al_2O_3 for every 33 cc. of the foregoing solution, and was brushed on to deposit a layer thickness containing about 600 milligrams of non-volatiles per square centimeter of surface. The resulting layer was also permitted to dry.

The slurries were shaken before dipping and before the brushes used for brushing were dipped into them. A little shaking keeps the slurries well dispersed for the few minutes needed to do the dipping or brushing, and each brush stroke applies a uniform slurry stratum that can be built up to the desired total layer thickness by an overlying brush stroke or two. Expert brush manipulation is not necessary.

The vanes with the dried three-layer masking on their roots were then packed in a chromizing powder pack in a plain carbon steel retort. An effective pack for this purpose is composed of a previously broken-in mixture of 40% Cr powder 1 to 10 microns in size, 59.5% alumina 10 to 20 microns in size, and 0.5% NH_4Cl powder. The pack is broken in by heating it for 10 hours at 2050°F under hydrogen in a retort without a workpiece, and then, after cooling, adding a fresh 0.5% NH_4Cl to make up for the driving off of the original NH_4Cl during the break-in.

The retort loaded with the masked blades packed in the chromizing pack, was then placed in an outer retort through which a protective gas was passed as described in U.S. Patent 3,785,854, and subjected to diffusion heat treatment bathed in hydrogen, the pack temperature reaching 2050°F where it was held for ten hours. A thermocouple embedded in the pack at a location into which the heat penetrates with greatest difficulty, was used to show the temperature.

After the packed retort has cooled down sufficiently it was removed from the outer retort and the workpiece unpacked. The masking was then in the form of a hard crack-free shell locked around each blade root. Striking this shell with a wooden mallet or rod breaks the shell into small pieces that do not adhere to the workpiece, and drop off revealing a smooth bright root surface free of chromized case. The balance of the blade showed a good chromized case 4 mils deep.

Similar results were obtained with other chromizing packs and using diffusion coating temperatures as high as 2200°F and as low as 1550°F. The same three-layer masking combination is also suitable for masking the blades against diffusion aluminizing, and even at aluminizing temperatures as low as 900°F such combination forms the hard shell that remains in place and keeps the masking from significantly contaminating the surrounding diffusion coating pack.

Such hard shell protection is also formed when the first of the three masking layers, that is the essentially inert layer, is omitted, but the masked workpiece surface is then apt to be not quite as smooth and bright, particularly when the diffusion coating is effected at very high temperatures. With or without the essentially inert layer, at least about 50 milligrams of Ni_3Al or similar nickel aluminide per square centimeter of masked surface assures the most effective masking, and this can be applied with or without the metallic chromium, and with or without the alumina or other inert diluent in the masking layer. When used without the chromium and without the foregoing first layer, some loss of chromium takes place from masked superalloy surfaces. Without the inert diluent the masking layer becomes more expensive unless its thickness is increased so that more care is needed to assure its proper application.

In general, a slurry used to apply a masking layer should have at least about 20 volume percent and up to about 70 volume percent of solid particles.

For diffusion aluminizing at temperatures below 1100°F or diffusion chromizing at temperatures below 1900°F, masking is very effectively provided without the first layer and without significant roughening of the masked surface. When masking workpiece surfaces of cobalt or cobalt-base alloys, cobalt aluminides can be used in place of nickel aluminides.

In general, the masking layer should contain powdered nickel or powdered

40% Metall

nickel aluminide or powdered cobalt aluminide, preferably diluted so that it constitutes up to about 90% of the layer, and at least about 25% of the layer, by weight. However, for masking superalloys, where depletion is to be avoided, elemental nickel should not be used in a layer contacting the masked surface or having only an essentially inert layer between it and the masked surface. In such use the masking ingredient should be a nickel or cobalt aluminide having between 1/3 and 3/4 atom of aluminum for every atom of nickel or cobalt.

The foregoing percentages do not take into account the resin bonding agent and the like that holds the layers in place but is driven off during the diffusion coating.

The second of the masking layers can be omitted and only the first and third layers used when masking against aluminizing and particularly when aluminizing stainless or low alloy steels.

The sheath-forming layer can be used as a very effective mask without any other helping layers, when aluminizing at temperatures below 1100°F. Sheath formation seems to be caused by the sintering together of the nickel particles in the third masking layer, under the influence of the diffusion atmosphere which causes diffusing metal to diffuse into the nickel of these particles. These particles thus grow in size. The Cr_2O_3 particles appear to form some chromium metal that becomes aluminized and sinters to a sheath.

Sheath formation can also be effected by adding to the sheath-forming layer a metal powder like aluminum the particles of which sinter to the nickel particles. Excessive addition is to be avoided to keep the added metal from contaminating the workpiece. Thus an aluminum addition of this type should contribute no more than about one atom of aluminum for every atom of nickel. As little as one one-hundredth of that proportion of aluminum helps the sheath formation, particularly where only a light diffusion is being performed.

The sheath-forming layer can be used to lock masking mixtures about a workpiece surface by partially or completely enveloping that surface. However such sheath formation will also securely hold a masking mixture against a portion of a flat or concave workpiece surface, particularly when such a combination is embedded in a powder pack in a diffusion coating retort.

Other inert diluents such as kaolin or MgO can be substituted for some or all the alumina in each of the foregoing formulations.

The fragments of sheath broken away from the workpiece after the diffusion coating is completed, can contain large quantities of nickel, and such nickel can be recovered from the fragments, if desired, as by dissolving it out in acid and separating the dissolved nickel from dissolved aluminum by ammoniacal precipitation of the aluminum. Alternatively, the fragments can be crushed into powder, their inert diluent such as alumina separated from the crushed powder by dropping that powder through a horizontally moving airstream that deflects the less dense diluent more than the more dense metal, melting the resulting metal with sufficient freshly added aluminum or nickel to convert the melt to Ni_3Al for reuse as such.

Omitting the stearic acid from the slurries used to apply the masking layers makes it more difficult to keep the slurries uniformly suspended and calls for the slurries to be shaken frequently to reduce settling.

Using the first and/or second masking layers without the third layer causes the applied masking layer or layers to develop cracks and gaps during the diffusion heating as a result of the thermal driving off of the binder resin. This causes the masking to be unreliable.

Omitting the nickel from the outermost of the three layers prevents it from forming the desired protective shell, unless the omitted nickel is replaced by Cr_2O_3 . The remaining ingredients of the outermost layer make it more generally effective and easier to apply, but are not essential.

The substitution of other acrylic resins such as poly(ethyl acrylate) or similar binder resins for the poly(ethyl Methacrylate) of Example 1 does not materially change the result. Methyl chloroform has a combination of non-flammability, volatility and lack of health hazard, that makes it particularly desirable.

The outermost or sheath-forming layer of the masking combination makes a very effective retaining or securing means that assures the locking of other types of layers beneath it onto the workpiece surface through the coating heat. The same secure action can be used to hold a slurry coating layer instead of a masking layer onto the workpiece, instead of the masking layer. This is illustrated in the following

example and makes it unnecessary to have the workpiece embedded in a coating pack.

Example 4

(In this Example, during the aluminizing of the exterior of a tube, the interior is simultaneously chromized by the method described and claimed in our copending Application No. 3218/79 (Serial No. 1,586,502).

A 5-foot length of steam generator high pressure tubing of Croloy alloy (1.9 to 2.6% Cr, 0.97 to 1.13% Mo, 0.15% C, balance essentially iron) having a 3/4 inch bore and a 1/2 inch wall was thoroughly cleaned inside and out, and had its bore filled with a chromizing pack composed of a previously broken-in mixture of

10% chromium powder the particle sizes of which range from about 10 to about 20 microns, and

90% tabular alumina granules having a particle size ranging from about 100 to about 300 microns

to which mixture was added 1/2% NH_4Cl granules as an activator. The breaking-in was effected by a mixture of the foregoing three ingredients in a retort in the absence of a workpiece, to 1800—1850°F for 10 hours under hydrogen. The tube so filled had its ends capped with 1010 steel caps frictionally fitted over the tube ends so as to provide semi-gas-tight covers.

The outside surface of the tube was then painted with the following layers in succession, drying the first layer for a few minutes before applying the second.

first layer—600 grams of a previously broken-in mixture of 45% Cr, 45% alumina and 10% Al, to which 1/2% NH_4Cl is added before as well as after break-in as described in U.S. Patent 3,801,357, suspended in 200 cc of methyl chloroform solution containing 7 weight percent of a copolymer of 70% ethyl and 30% methyl methacrylates, 0.5 weight percent stearic acid and 0.1 weight percent cetyl ether of decaethoxy ethanol. Four applications of this mixture are made with intervening drying to build the non volatile coating to 1200 milligrams per square centimeter of tube surface.

second layer—600 grams of a mixture of 68.5% Ni powder and 31.5% Al powder, dispersed in 150 cc of above methyl chloroform solution. The metals of this slurry were not pre-fired, and only two applications of this slurry was made to provide a non-volatile coating weight of about half that of the first layer.

The tube so prepared was placed in a tubular retort of a diffusion coating furnace assembly having inlet and outlet connections for a hydrogen-blanketing as in U.S. Patent 3,801,357 and then subjected to a diffusion coating heat of 1800°F for 10 hours. After cooldown at the end of the heat the tube end caps were removed, the pack in the tube bore poured out, and the sheath around the exterior of the tube broken off and removed. The interior of the tube was effectively chromized with a case 1.8 to 2.3 mils thick, and the outside of the tube aluminized with a case about 24 mils thick.

The chromized case included an outer portion about 0.3 mil thick rich in chromium carbide, and an inner portion of columnar chromized structure. This case is particularly effective in reducing erosion of the internal tube surface by rapidly moving high pressure steam.

The aluminized outer surface prolongs the life of the tube in a coal—or oil-fired furnace where it is subjected to combustion atmosphere at temperatures as high as about 1000°F.

The internal pack is a highly fluent composition that is easily poured into place before the heat, and is readily removed afterwards, using a minimum of mechanical poking and the like. Such a pack is particularly desirable for packing of cramped recesses in the interior of workpieces, such as in the narrow bores described above, or in hollow jet engine blades, or the like. Its use is described and claimed in our copending Application No. 3218/79 (Serial No. 1,586,502).

Any ferrous base steam boiler tubing is improved by the foregoing diffusion coatings. Plain carbon and low alloy steels will form the chromium carbide stratum with underlying columnar chromized case, and will show very little abrading loss when used with high pressure steam. Such abrasion by the steam causes the steam to carry along with it the abraded particles and they can damage the vanes and blades of turbines driven by the steam. For such pressurized use the boiler tubing should have a wall thickness of at least about 3/16 inch.

The external surfaces of boiler tubing are also made more resistant to

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10 10% Metall

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55% Metall

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corrosion as a result of the aluminizing or the chromizing described above, even the minor chromizing effected when only the interior of such a tube is packed with the diffusion chromizing mix.

As pointed out, the shell-forming layer used to hold a slurry coating in place where there is not much of an aluminizing or chromizing atmosphere, contains non-contaminating materials that sinter together under coating conditions. Thus nickel and aluminum powders smaller than about 500 microns in size and in an atom proportion from about 1:0.9 to about 1:1.1 are very effective. Chromium can be substituted for the nickel in such a mixture. Because of the non-contaminating character, a diffusion coating pack will not be ruined in the event a small amount of the masking materials should inadvertently become mixed into it.

The foregoing inner and outer coatings can be applied to tubes as long as 40 feet or more in length, whether those tubes be straight or cane-shaped. For such long tubes it is desirable to effect the diffusion coating uniformly along the tube lengths, and to this end the diffusion coating temperature along the length of the tube can be closely controlled. Thus a plurality of the tubes each with its bore packed and its ends capped can be inserted lengthwise in a tubular open-ended retort sufficiently narrow to make a snug container for the tubes. One or more of the tubes is also fitted with a number of thermocouples on its exterior and distributed along its length. The retort so loaded can then be inserted in a furnace having a number of gas burner rings spaced along the retort's length, each ring encircling the retort. Only one end of the retort need be open, and that end can be sealed with a head that has a number of passageways. Some of these passageways are used for the passage of thermocouple connection wires, and two can be used as inlet and outlet respectively, for a bathing gas such as hydrogen.

The operation of the burner rings is then adjusted to bring all the thermocouples to the desired temperature. Should there be a temperature variation among the thermocouples, individual burners can be further adjusted. In this way a cool thermocouple can have its temperature brought up by turning up the nearest burner or burners, and conversely a hot one can have its temperature reduced by turning down the nearest burner or burners. These control functions can be effected manually or automatically to maintain the temperature of the packed tubes within a range of about 25°F along their entire lengths.

Cane-shaped tubes can be handled the same way. Also an argon washing atmosphere can be maintained throughout most or all of the diffusion coating of Example 4 without significantly different results. Because of its expense, the flow of argon should be reduced to a very small rate by back pressuring it equivalent to 1 to 2 inches of water. Alternatively, that diffusion can be effected in a glass-sealed retort with an autogeneously generated atmosphere.

Fluent diffusion coating packs are also helpful for use with the shell-forming masking arrangements described above. Such coating packs do not have to be mechanically worked to loosen them after a coating heat is completed, and there is accordingly less danger of damage to the masking shell.

Any of these retort and retort atmosphere arrangements can also be used with slurry coatings or conventional packs to aluminize nickel, platinum and other metals for the purpose of improving their catalytic activity as described in U.S. Patent 3,867,184. Part of the metal surface can also be masked as by the sheath-forming layer directly applied to those parts. When a nickel surface of high catalytic activity is desired, the nickel is best subjected to diffusion aluminizing in a plurality of stages before the leaching. In the first diffusion stage the activity of the inwardly diffusing aluminum is kept low as by using an aluminum diffusion pack containing 10 to 40% aluminum, the balance alumina, with a 0.3% AlCl_3 energizer added. A diffusion treatment of 1050 to 1100°F for 20 to 30 hours with such a pack causes the formation of the nickel surface of an aluminized case in which essentially all its aluminum is in the form of Ni_2Al_3 intermetallic.

In a subsequent diffusion aluminizing stage the outer portion of the aluminized case is modified to convert the Ni_2Al_3 to a higher aluminide of nickel. The aluminizing pack of the first stage can be used in a second stage conducted at a lower temperature, as for example from about 880 to about 920°F, for 20 to 30 hours as an effective technique for converting the aluminide in the outermost portion of the case to higher aluminide.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practised otherwise than as specifically described.

WHAT WE CLAIM IS:—

1. A method for localized chemical-vapor-diffusion-coating of metal into a portion of the surface of a metal workpiece, which method comprises applying to the workpiece, at least one adherent chemical-vapor-deposition-delineating layer that delineates the area of the surface to be diffusion coated, the layer being applied as a slurry of chemical-vapor-diffusion-delineating powder in a solution of a heat-fugitive resin binder in a solvent which is methyl chloroform or methylene chloride permitting the solvent to evaporate to set the layer, and then subjecting the thus-coated workpiece to chemical vapor diffusion coating. 5
2. A method as claimed in claim 1, wherein the chemical-vapor-deposition-limiting layer prevents diffusion coating of the workpiece in the area to which the said layer is applied. 10
3. A method as claimed in claim 2, wherein the chemical-vapor-diffusion-delineating powder comprises powdered nickel and/or Cr_2O_3 . 15
4. A method as claimed in claim 2 or claim 3, wherein the said layer comprises an inert diluent. 15
5. A method as claimed in claim 4, wherein the inert diluent is alumina.
6. A method as claimed in claim 1, wherein the chemical-vapor-deposition-delineating layer contains the metal with which the said portion of the workpiece surface is to be diffusion coated, whereby the area of the surface covered by the layer becomes diffusion coated with the said metal, during the diffusion coating process. 20
7. A method as claimed in Claim 6, wherein the diffusion-delineating powder comprises powdered chromium and/or powdered aluminium. 25
8. A method as claimed in any one of the preceding claims in which the binder comprises an acrylic resin. 25
9. A method as claimed in any one of the preceding claims, wherein the slurry includes a quantity of a dispersing aid.
10. A method as claimed in claim 9, wherein the dispersing aid is a long-chain hydrocarbon acid. 30
11. A method as claimed in any one of the preceding claims, wherein a plurality of superposed adherent chemical-vapor-deposition delineating layers are applied to the workpiece.
12. A method as claimed in claim 1 and substantially as hereinbefore described in any one of the Examples. 35

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